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CHAPTER 1

THE ADSORPTION PROCESS USING CUSTARD APPLE (ANNONA SQUAMOSA) SEEDS FOR THE REMOVAL OF CHEMICAL OXYGEN DEMAND AND TURBIDITY

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1.1 INTRODUCTION

River is considered as the most important freshwater source for human. Major rivers are used for drinking water supply, irrigation of agricultural lands, industrial and municipal water supplies, industrial and municipal water supplies. Water cannot be used directly from the sources due to the presence of contaminants [1]. Water used for drinking purpose should meet the water quality standards in the term of physical, biological and chemical characteristics. Therefore, effective water treatment is needed to improve the quality of water [2].

There are many parameters can be used to determine the water quality. These includes Chemical Oxygen Demand (COD) and turbidity of water. COD is a measure of oxygen consume by bacteria for decomposition of organic matter and the oxidation of inorganic chemicals. High level of COD in water affects human health by the presence of bacteria that degrade organic wastes in the water. Microorganisms that include viruses, parasites and bacteria in the water can cause waterborne diseases if consume such as nausea, cramps, diarrhea and headaches. High level of COD will decrease the amount of dissolved oxygen available for aquatic lives. Dissolved oxygen under 3 mg/L can cause hypoxia that reduce cell functioning, disrupts circulatory fluid balance in aquatic species and results in death of organisms [3].

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Turbidity is the amount of cloudiness or haziness in the water. High turbidity can also cause low oxygen level due to the excessive content of suspended particles in the water. Murky water hinders aquatic livings from searching their food and breeding. In addition, turbidity can reduce light penetration and decrease algae growth. Low algae productivity as food source will decrease the population of many aquatic invertebrates [4].

Many treatments had been used to treat the water but most of them are costly. One of the most economical ways to treat water is by adsorption process. The use of low cost adsorbent has becoming popular among researcher since it is economical with good performance [5]. Adsorption is a process that bonds atoms, ions or molecules in gas, liquid or solid state through the surface area of the adsorbent. It is an effective removal process for many contaminants in water treatment. Adsorbate is the compound that accumulates at the interface while adsorbent is solid compound on which adsorption occurs [6]. On the surface of solids, there are unbalanced forces of attraction which are responsible for adsorption process to occur. It is called physical adsorption or physisorption is when the adsorption is take place due to weak van der Waals forces. Chemical adsorption is the chemical bonding between adsorbent and adsorbate molecule [7]. The physical adsorption involves only weak intermolecular forces, while chemical adsorption involves the chemical bond between the sorbate molecule and the surface of adsorbent. The small particle sizes of adsorbents allow high rates of adsorption and short contact times to reach adsorption equilibrium.

There are three consecutive steps proposed in the mechanism of adsorbents. First, the solute transports from bulk solution through a liquid film to the outer surface of carbon. Second, the solute diffuses into pores of the adsorbent except for a small quantity of adsorption on the outer surface. Third, there is adsorption of the solute on the inner surfaces of the pores and capillary spaces of the adsorbent. This last step is considered to be an equilibrium reaction. This sequence leads to an adsorptive capacity for solutes on carbon adsorbent [8]. Advantages of adsorption process are potential for many contaminants removal, flexibility in design, simple process, low cost and do not produce toxic products. However, adsorption process also has the drawback as adsorbent regeneration process require steam or vacuum source that can be costly to desorb high molecular weight pollutants [9].

The effectiveness of adsorption is determined by the types of substances to be removed. Substances with a high molecular weight and low water solubility are better adsorbed with activated carbon. The effectiveness of adsorption is also influenced by the concentration of the substance, the presence of other organic components, adsorbent dosage, temperature and pH [10]. Almost 90% of water treatment plants use activated carbons in powdered forms for adsorption processes. Apart from that, various agricultural wastes have been explored as low-cost adsorbents such as coconut husk, rice husk, palm oil husk, durian peel, orange peel and many more. One of the natural adsorbents with great potential is custard fruit. Krishna and Sree [11] had proved that custard apple peel powder can be used to remove hexavalent chromium. A study by Equbal et al. [12] also proved that custard apple peel powder can be used to adsorb methyl red. While, Parate et al. [13] showed that the seeds from custard apple can be used to remove Ni^{2+}.

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1.2 WATER QUALITY PARAMETERS

Water quality testing is important in environmental monitoring. There are many parameters that will affect the quality of water in the environment. These parameters can be categorized as physical, chemical or biological. Physical parameters include temperature, turbidity, taste and odor. Chemical parameters include pH, dissolved oxygen (DO), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). While for biological parameters are algae, phytoplankton and bacteria. These parameters are commonly tested in water source [14].

The water quality parameters can be classified based on the National Water Quality Standards for Malaysia shown in Table 1.1. The water should be classified based on the concentration range of the parameter tested. The water for class I had the lowest tolerable concentration parameters that should be met, which is used for drinking purposes. While water for class V had the highest concentration parameters which indicate the water is not acceptable for drinking purposes.

Table 1.1: National Water Quality Standards for Malaysia [15]

Parameter	Unit	Class					
		I	IIA	IIB	III	IV	V
Ammoniacal Nitrogen	mg/l	0.1	0.3	0.3	0.9	2.7	>2.7
Biochemical Oxygen Demand	mg/l	1	3	3	6	12	>12
Chemical Oxygen Demand	mg/l	10	25	25	50	100	>100
Dissolved Oxygen	mg/l	7	5-7	5-7	3-5	>3	>1
pH	-	6.5-8.5	6-9	6-9	5-9	5-9	-
Color	TCU	15	150	150	-	-	-
Electrical Conductivity	µS/cm	1000	1000	-	-	6000	-
Floatables	-	N	N	N	-	-	-
Odor	-	N	N	N	-	-	-
Salinity	%	0.5	1	-	-	2	-
Total Dissolved Solid	mg/l	500	1000	-	-	4000	-
Total Suspended Solid	mg/l	25	50	50	150	300	300
Temperature	ºC	-	+2 ºC	-	+2 ºC	-	-
Turbidity	NTU	5	50	50	-	-	-

1.3 CUSTARD APPLE (ANNONA SQUAMOSA)

Custard apple or sugar apple (*Annona Squamosa)* is a type of fruit, approximately 5 to 10 cm in diameter and weighing in between 100 to 240 gram. It has a thick skin composed of knobby segments. The colour of the peel is typically pale green, with a deep pink, reddish

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or brownish-red blush. It is unique that *Annona* fruits segments tend to separate when ripe, exposing the interior. The flesh is fragrant and sweet, creamy white in colour, resembles custard. It is found adhering to 13 to 16 mm long seeds forming individual segments arranged in a single layer around a conical core. The fruit is soft, slightly grainy, and slippery. The seeds may contain from 20 to 40 for one fruit [16]. The seeds can be eaten but the kernels are toxic as it has insecticidal and abortifacient properties. Figure 1.1 shows the custard apple fruit.

Figure 1.1: Custard apple fruit

The custard apple seed extracts contain carboxyl group (–COOH) and hydroxyl group (–OH) that can form bonding with contaminant in the adsorption process. Besides that, the seed extracts have been reported by several researchers for their antimicrobial effects activity [17]. This is due to the presence of certain substances such as alkaloids, glycosides, tannins, volatile oils, gums, steroids, saponins, flavonoids and phlobatannins [18]. It is effective against some bacteria such as Staphylococcus aeureus, Vibrio cholera and Escherichia coli in water bodies.

Custard apple contains polysaccharides which are capable to reduce the COD and turbidity in water. Polysaccharides such as chitin [19], starch [20], chitosan [21] and cyclodextrin [22] deserve particular attention. These biopolymers represent an interesting alternative as adsorbents due to present of their particular structures, chemical stabilities, physico-chemical characteristics, high reactivity and excellent selectivity towards aromatic compounds and metals. This is resulted from the presence of functional groups such as hydroxyl, acetamido or amino groups in polymer chains. Polysaccharides are abundant, renewable and biodegradable resources. They have a capacity to associate by physical and chemical interactions with a wide variety of molecules [23]. Hence, adsorption on polysaccharides is a low-cost procedure in water decontamination for extraction and separation of compounds.

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1.4 POTENTIAL USED OF CUSTARD APPLE (ANNONA SQUAMOSA) AS ADSORBENT

There is a recent interest in the synthesis of new adsorbents containing polysaccharides had been shown due to the increasing number of publications on adsorption of toxic compounds by using these natural polymers [24]. According to Krishna and Sree [11], the removal of hexavalent chromium, Cr (VI) by using custard apple peel powder as adsorbent was examined in the batch experiments with different content times, adsorbent dosage, temperature, initial chromium concentration and the pH solution. The maximum chromium uptake is found to be 7.874 mg/g. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis confirm the binding of chromium on adsorbent surface. The results obtained show that custard apple peel powder is an effective and economical adsorbent for removal of hexavalent chromium from industrial waste water.

Equbal et al. [12] investigate the removal of methyl red by using custard apple peel powder as activated carbon by K_2CO_3 and H_3PO_4 activation. The contact time, adsorbent dose, initial concentration of methyl red, pH and temperature were optimized by batch method. The Langmuir adsorption capacity, Qm for $ACPO_4$ (435.25 mg/g) was found to be higher than that for $ACCO_3$ (226.90 mg/g). Both of the adsorption efficiency of $ACCO_3$ (61%) and $ACPO_4$ (64%) are moderate.

For the study of using custard apple seeds to remove Ni (II) by Parate et al. [13], the effectiveness of custard apple seeds as adsorbents to remove Ni (II) is depends on the pH, agitation speed, contact time, temperature and adsorbent dosage. In optimum condition of pH of 8.0, agitation speed of 200 rpm, 500℃ and 240 minutes, minimum amount of custard apple seeds adsorbents are required to remove almost all the Ni (II) from solution which is 50 mL with the efficiency of 85.6 %.

Apart from that, Santhi et al. [25] also proved that custard apple seeds can be used to remove methyl blue, methyl red and malachite green dyes from wastewaters. Adsorption of the three types on custard apple seeds showed highest values at around pH 7 with percentage adsorbed around 20 %, 40 % and 90%.

1.5 METHODOLOGY

Custard apple (Annona squamosa) are used as adsorbents to treat river water. Two types of parameters are selected for testing the efficiencies of custard apple seeds as adsorbents, which are COD and turbidity. Batch adsorption study is used to determine adsorption process. The testing of COD and turbidity is performed based on APHA standard method. The samples of river water are collected from Simpang Kiri River to be tested for water quality parameters. For Water Quality Index (WQI) testing, water sample was taken from Panchor River and six parameters are tested. This included COD, pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), total suspended solids (TSS) and ammonia nitrogen (NH_3-N). Figure 3.1 shows the flowchart methodology of this study.

1.5.1 Collection of water samples

The water samples are collected from Simpang Kiri River and Panchor River. Different water quality parameters such as pH, temperature, DO, turbidity and BOD are measured in-situ. Hanna portable waterproof dissolved oxygen meter is used for measurement of DO and temperature. Hanna multi-parameter water quality portable meter is used for measurement of BOD. Hanna portable pH meter is used for measurement of pH while Hanna TL 2300 turbidity meter is used for the measurement of turbidity. For ex-situ parameter such as COD is measured by using Hanna DR 6000 spectrophotometer. The water samples are filtered first by using filter paper to remove any impurities before starting the adsorption experiment.

1.5.2 Preparation of custard apple seeds as adsorbents

The custard apple seeds are washed with tap water to remove any dirt. The seeds were then washed with double distilled water. After that, the seeds were dried in hot air oven at 105℃ for 6 hours. Then, the seeds were cooled in desiccator. The activation of dried seeds was by using 10% H_2SO_4 solution by shaking at 200 rpm for 4 hours at room temperature. The produced adsorbents were washed with double distilled water several times until it reaches to neutral pH. Then, the seeds were dried in oven at 85℃ for 2 hours. After that, the crushing and sieving of the dried materials was done to get particle sizes of 150 to 250 µm. The final products are stored in air tight container [13].

The method chosen was dried the custard apple seeds under the sun for five days. Then, the seeds were crushed into small pieces. The seeds were putted into furnace for heated around one hour at 500℃. The seeds were cooled until room temperature and then crushed into fine powdered form. After that, the seeds were sieved to get particle sizes of 150 to 250 µm.

1.5.3 Batch adsorption study

Batch adsorption study was conducted to find the adsorption capacity and optimum adsorbent dosage. The adsorbents were weighted according to different dosage as shown in Table 1.2 and placed into each 250 mL conical flask using a spatula. Then, the conical flasks were filled with 200 mL of water samples except for the blank sample was filled with distilled water. The initial reading for COD and turbidity was measured.

Table 1.2: Different adsorbent dosage.

Conical flask number	1	2	3
Adsorbent mass (g)	0.1	0.5	1
Adsorbent concentration (mg/L)	500	2500	5000

After that, the samples were placed on an orbital shaker to provide agitation at constant stirring speed of 230 rpm at room temperature. The reading for COD and turbidity was measured at certain time interval by using DR 6000 spectrophotometer and Hanna TL

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2300 turbidity meter respectively. The removal and adsorbed capacity of COD and turbidity were calculated using the following equations 1.1 and 1.2 below:

$$R_t = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1.1)$$

$$Q_t = \frac{C_0 - C_t}{m} \times V \quad (1.2)$$

where, R_t is the COD or turbidity removed by the adsorbent at the time t (%).
C_0 is the initial concentration of COD or turbidity solutions (mg/L).
C_t is the concentration of COD or turbidity solutions at time t (mg/g).
Q_t is the adsorbed COD or turbidity amount per gram of the adsorbent powder at the time t (mg/g).
V is the volume of the sample (L).
m is the mass of the adsorbent (g).

1.5.4 Water quality index testing

Batch adsorption study was conducted to find the WQI of the water before and after treatment. The adsorbents were weighted to one gram and placed into a 250 mL conical flask using a spatula. Then, the conical flask was filled with 200 mL of water sample. The initial readings for COD, pH, DO, BOD, TSS and NH_3-N were measured.

After that, the sample was placed on an orbital shaker to provide agitation at constant stirring speed of 230 rpm at room temperature for one hour. The final readings for six parameters were measured after treatment by using DR 6000 spectrophotometer, pH meter, DO meter, Hanna TL 2300 turbidity meter and weighing balance. Water Quality Index (WQI) of the water samples before and after treatment was calculated by using the formula shown below and compared based on Table 1.3:

WQI=(0.22*SIDO)+(0.19*SIBOD)+(0.16*SICOD)+(0.15*SIAN)+(0.16*SISS)+(0.12*SIpH) (1.3)

Where;
SIDO = Sublndex DO (% saturtlon)
SIBOD = Sublndex BOD
SICOD = Sublndex COD
SIAN = Sublndex NH3-N
SISS = Sublndex SS
SipH = Sublndex pH
$0 \leq WQI \leq 100$

Sublndex for DO (In % saturation)
SIDO = 0 for $x \leq 8$
SIDO = 100 for $x \leq 92$
SIDO = $-0.395 + 0.030x^2 - 0.00020x^3$ for $8 < x < 92$ (1.4)

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Sublndex for BOD

$SIBOD = 100.4 – 4.2$ for $x \leq 5$ (1.5)

$SIBOD = 108\ e^{(–0.055x)} – 0.1x$ for $x > 5$ (1.6)

Sublndex for COD

$SICOD = –1.33x + 99.1$ for $x \leq 20$ (1.7)

$SICOD = 103\ e^{(–0.0157x)} – 0.04x$ for $x > 20$ (1.8)

Sublndex for NH_3–N

$SIAN = 100.5 – 105x$ for $x \leq 0.3$ (1.9)

$SIAN = 94\ e^{(–0.573x)}) – 5\ |x – 2|$ for $0.3 < x < 4$ (1.10)

$SIAN = 0$ for $x \geq 4$

Sublndex for SS

$SISS = 97.5\ e^{(–0.00676x)} + 0.05x$ for $x \leq 100$ (1.11)

$SISS = 71\ e^{(–0.0061x)} + 0.015x$ for $100 < x < 1000$ (1.12)

$SISS = 0$ for $x \geq 1000$

Sublndex for pH

$SlpH = 17.02 – 17.2x + 5.02x^2$ for $x < 5.5$ (1.13)

$SlpH = –242 + 95.5x – 6.67x^2$ for $5.5 \leq x < 7$ (1.14)

$SlpH = –181 + 82.4x – 6.05x^2$ for $7 \leq x < 8.75$ (1.15)

$SlpH = 536 – 77.0x + 2.76x^2$ for $x \geq 8.75$ (1.16)

Table 1.3: Water quality index

Range	Quality
90 – 100	Excellent
70 – 90	Good
50 – 70	Medium
25 – 50	Bad
0 – 25	Very bad

1.6 RESULTS AND DISCUSSIONS

1.6.1 Fourier Transform Infrared Spectroscopy (FTIR) analysis

The infrared spectrum of absorption or emission of custard apple seeds adsorbents are obtained by determining the peak and intensity wavenumbers of custard apple seeds adsorbents. FTIR spectra of the custard apple seeds adsorbents is shown in Figure 1.2 below. The peak at 1574 shows the functional groups that existed in the absorbance which are carboxyl group (C=O) stretching while peak of 3265 is due to hydroxyl group (-OH) stretching and transmittance at 2922 is due to –CH stretching. This shows that the adsorbent contains carboxyl group, hydroxyl group and alkyl group (-CH_3) that are responsible for adsorption process of contaminants.

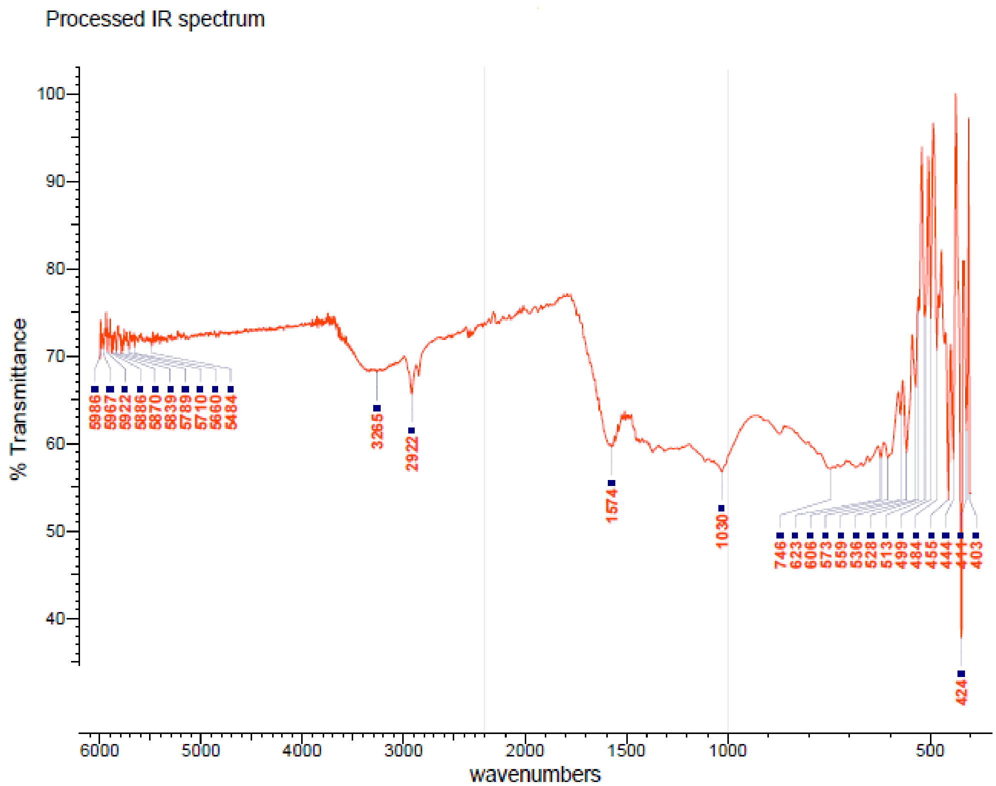

Figure 1.2: FTIR spectra of the custard apple seeds adsorbents

1.6.2 Removal and adsorbed capacity of turbidity

The results of both Rt and Qt for turbidity are plotted into Figure 1.3 and Figure 1.4, respectively. It can be seen that both Rt and Qt are increased as the readings of turbidity decreased along the time. By using 0.1 gram of adsorbent, it can reduce turbidity from the water sample up to 87 %. For 0.5 gram of adsorbent, it can reduce the turbidity present in water up to 96 % in 240 minutes. While for 1 gram of adsorbent used, the ability of removal of turbidity increased to 92% at 60 minutes or 1 hour, but suddenly drops to 89 % at 120 minutes and 240 minutes. For the amount of turbidity adsorbed, the adsorbent can only adsorb up to 13.580 mg/g, 2.989 mg/g and 1.386 mg/g by using 0.1 gram, 0.5 gram and 1 gram of adsorbents respectively after 240 minutes of batch adsorption process.

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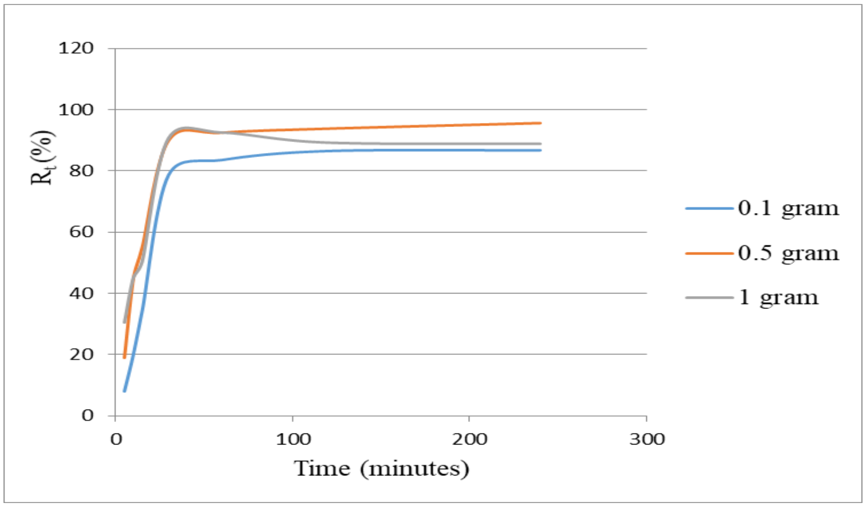

Figure 1.3: Turbidity removal versus time

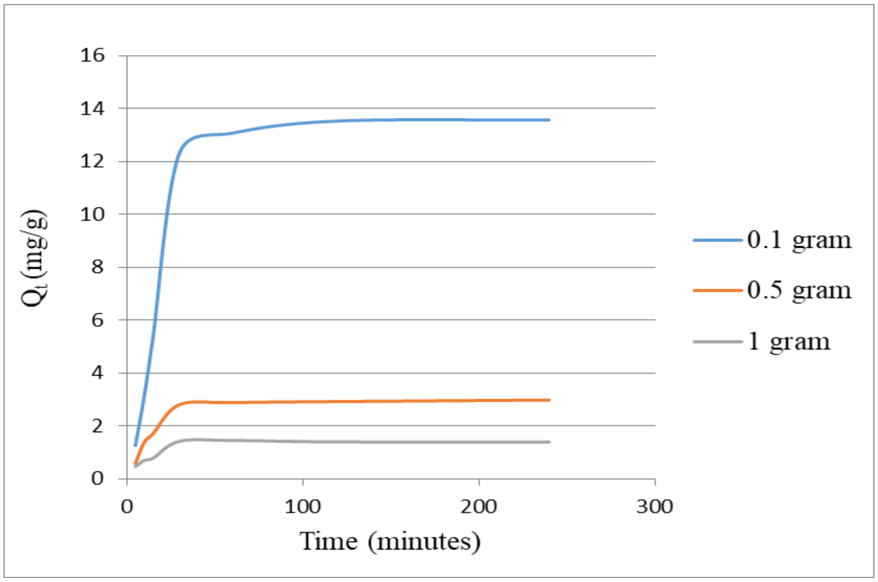

Figure 1.4: Turbidity adsorb versus time

1.6.3 Removal and adsorbed capacity of COD

The results of both Rt and Qt for COD are tabulated into Figure 1.5 and Figure 1.6, respectively. From the results obtained above, both Rt and Qt are increased as the readings of COD decreased along the time. By using 0.1 gram of adsorbent, it can reduce COD from the water sample up to 75 %. While for 0.5 gram of adsorbent used, it can also reduce COD present up to 85 %. By using 1 gram of adsorbent, 91 % of the COD had been removed from the water when the batch adsorption process undertaken 240 minutes. For the amount of COD adsorbed is about 100 mg/g when 0.1 gram of adsorbent is used. Whereas for 0.5

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gram and 1 gram of adsorbents used, only adsorb up to 22.668 mg/g and 12.068 mg/g respectively after 240 minutes.

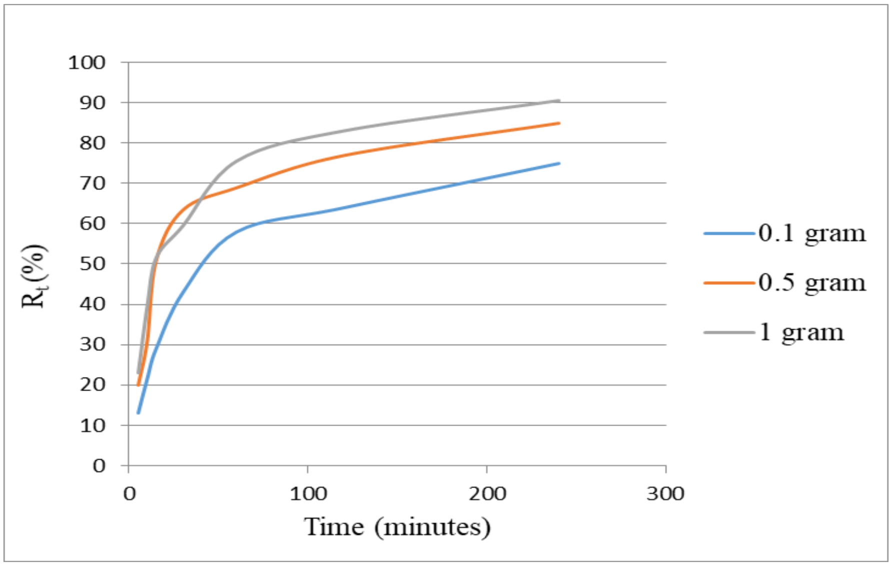

Figure 1.5: COD removal versus time

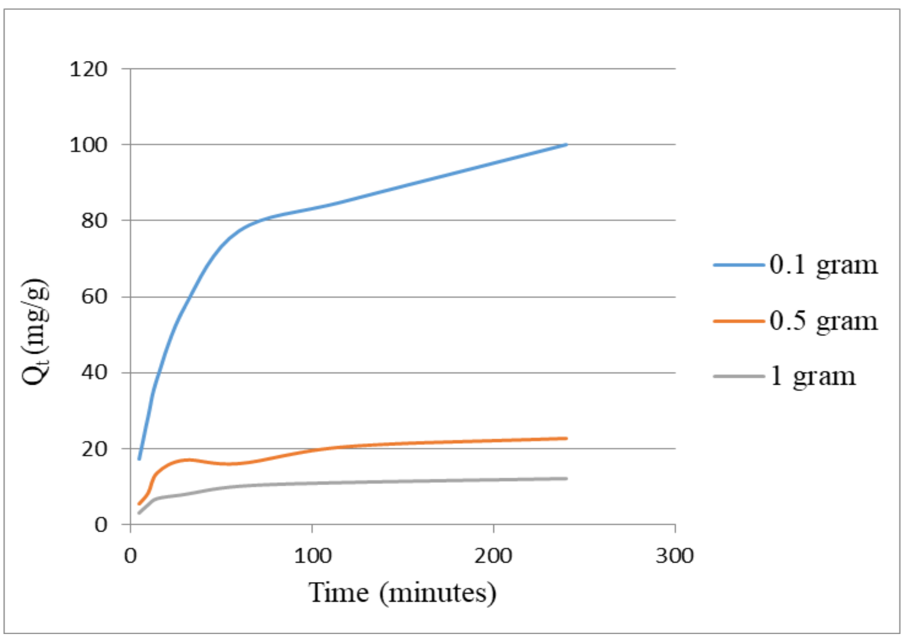

Figure 1.6: COD adsorb versus time

1.6.4 Water quality index (WQI)

Batch adsorption method is conducted by using powdered custard apple seeds as adsorbents. The initial readings of six different parameters of the water sample taken from Panchor River are tested. These six different parameters are pH, dissolved oxygen (DO), chemical

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oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS) and ammonia nitrogen (NH_3-N). The readings are taken after one hour of adsorption process. The data obtained are tabulated into Table 1.4.

Table 1.4: Initial and final readings of six different parameters in water sample

Reading	pH	DO (mg/L)	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	NH_3-N (mg/L)
Initial	6.30	9.10	30.00	3.00	16000	1.02
Final	8.86	7.50	2.00	5.00	4200	0.92

From the table above, pH increases from 6.30 to 8.8.6. Both dissolved oxygen (DO) and chemical oxygen demand (COD) decrease from 9.10 mg/L to 7.15 mg/L and from 30.00 mg/L to 2.00 mg/L, respectively. For biochemical oxygen demand (BOD), both 10 mL and 40 mL samples used are increased by 2.00 mg/L. For total suspended solids (TSS) and ammonia nitrogen (NH3-N) are decrease from 0.80 gram to 0.21 gram and from 1.02 mg/L to 0.92 mg/L, respectively.

The increase in pH level was due to the present of organic materials in the adsorbents used. The decrease in DO level from 9.10 to 7.50 was due to increase in BOD level. This is because the oxygen available in the water has being consumed by the bacteria present in the water. COD is decreased as the adsorbents adsorb the contaminants from the water, and thus, decreased in TSS. The decrease in NH_3-N was due to decreasing acidic of the water as pH increases to 8.86 which is weak basic. According to water quality index legend as shown in Table 1.3, the quality of the water before treatment is 43.677 which can be categorized as bad. Suprisingly, after treatment using the adsorbent, the WQI is 44.460 which is also bad although after treatment. This might be due to the saturation of the organic contaminants onto the adsorbent that reduces the efficiency.

1.7 CONCLUSION

In conclusion, the custard apple seeds adsorbents had been proved to have the abilities to remove COD and turbidity from river water. The adsorbents had the abilities to remove COD and turbidity as higher as 90.5% and 95.6 % respectively. According to National Water Quality Standards for Malaysia, after treatment by using custard apple seeds adsorbents, the water from Simpang Kiri River still needed some conventional treatment prior to consumption. While for WQI testing and treatment of Panchor River, it only had minor changes which was from 43.677 to 44.460 and can be classified as bad quality of water. From the results obtained, the custard apple seeds adsorbents had the abilities to remove contaminants from the water, but had low WQI as the seeds decreased dissolved oxygen content and increased biochemical oxygen demand.

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